

## Optimized preparation conditions of yttria doped zirconia coatings on potassium ferrate (VI) electrode for alkaline super-iron battery

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### HIGHLIGHTS

- $\text{Y}_2\text{O}_3$ – $\text{ZrO}_2$  coatings on  $\text{K}_2\text{FeO}_4$  electrodes are prepared.
- Super-iron coin cells are assembled using  $\text{Y}_2\text{O}_3$ – $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  electrode.
- The discharge property of super-iron coin cell is superior to  $\text{Zn}/\text{MnO}_2$  coin cell.
- Super-iron battery can substitute for present primary batteries in application.
- Alkaline super-iron battery is expected to become a novel energy resource system.

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### ABSTRACT

To enhance the stability of potassium ferrate (VI) ( $\text{K}_2\text{FeO}_4$ ) electrodes and their discharge capabilities in alkaline battery systems, yttria ( $\text{Y}_2\text{O}_3$ ) doped zirconia ( $\text{ZrO}_2$ ) (denoted as  $\text{Y}_2\text{O}_3$ – $\text{ZrO}_2$ ) coatings are utilized to protect the  $\text{K}_2\text{FeO}_4$  electrode in alkaline electrolytes. The preparation conditions of  $\text{Y}_2\text{O}_3$ – $\text{ZrO}_2$  coatings on  $\text{K}_2\text{FeO}_4$  electrodes are investigated in detail and the optimum preparation conditions are determined. Results of discharge tests with open module batteries show that the  $\text{Y}_2\text{O}_3$ – $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  electrode (prepared under the optimum conditions) provides a superior discharge specific capacity than uncoated and  $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  electrodes. Alternatively, to further explore the practical application of  $\text{K}_2\text{FeO}_4$  electrodes, super-iron coin cells are assembled using a  $\text{Y}_2\text{O}_3$ – $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  electrode as the cathode and zinc foil as the anode. The discharge specific capacity and discharge specific energy of the coin cell with  $\text{Y}_2\text{O}_3$ – $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode are  $169.8 \text{ mA h g}^{-1}$  and  $201.9 \text{ Wh kg}^{-1}$  respectively, which are superior to the  $\text{MnO}_2$  coin cell. Therefore, the results indicate that  $\text{Y}_2\text{O}_3$ – $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode is suitable for practical applications in alkaline battery systems. Consequently, the alkaline super-iron battery is expected to become a novel energy resource system that replaces present primary batteries in various electronic devices.

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### 1. Introduction

At present, our world is facing the progressive depletion of energy resources especially non-renewable fuels and severe environmental concern due to the consumption of fossil fuels for energy is being increased [1–5]. Therefore, it is indispensable for us to develop sustainable, environmentally benign and cost effective energy sources to meet future energy requirements. Energy based on electricity generated from electrochemical batteries is one of the most efficient, convenient and reliable power sources [6,7]

and is used in many fields including portable electronic consumer devices, medical implants, transportation, etc. [8,9]. Among all the electrochemical batteries under research, the alkaline super-iron battery has attracted great interest and been extensively studied in the recent two decades owing to its following attractive advantages [10–15], firstly, alkaline super-iron batteries possess high energy storage capacity (intrinsic three electron capacity) compared to traditional primary batteries which are made of heavy metal oxides with single or less than one electron redox chemistry; secondly, the alkaline super-iron battery has been known as a “green environmental-protective battery” owing to its non-toxic and colloidal Fe (III) discharge products; thirdly, the alkaline super-iron battery is a sustainable energy system for the discharge product ( $\text{Fe}_2\text{O}_3$ ) can be recycled and become the raw material of the

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super-iron battery. Therefore, to enhance energy storage density, mitigate environmental pollutants, and improve the sustainability of electrode material utilization of primary batteries, the alkaline super-iron battery is expected to become a novel energy resource and a substitute for present primary batteries in various electronic devices such as mobile electronics, and electric appliance.

Generally, the electrode material of super-iron battery is ferrate (VI), such as  $K_2FeO_4$ ,  $BaFeO_4$ ,  $CuFeO_4$ , and  $SrFeO_4$  electrodes [16,17]. Among these Fe (VI) electrodes,  $K_2FeO_4$  electrodes have been paid the most emphasis due to their higher solid-state stability (decomposition/each year is less than 0.1%) and high theoretical special capacity ( $406 \text{ mA h g}^{-1}$ ) [10,18]. However, commercial applications of alkaline super-iron batteries based on  $K_2FeO_4$  electrodes have not been implemented due to their chemical instability and self-discharge [19]. Especially, in alkaline battery systems, the formation of Fe (III) overlayer during storage is likely to deteriorate the charge transfer of  $K_2FeO_4$  electrodes. Meanwhile, the resulting Fe (III) overlayer will accelerate the decomposition of  $K_2FeO_4$  electrodes [20,21]. Hence, solving these existing disadvantages is a key step for bringing  $K_2FeO_4$  electrodes into practical application.

To improve the stability of the super-iron battery, ferrate electrodes coated by inorganic materials such as  $SiO_2$  and organic materials such as 2,3-Naphthalocyanine ( $C_{48}H_{26}N_8$ ) have been reported in the previous studies [19,20,22]. Licht et al have repeatedly investigated ceramic material of zirconia ( $ZrO_2$ ) used as protective coatings to stabilize the  $K_2FeO_4$  electrode [18,21,23], and their investigation results indicate that the  $ZrO_2$  coating significantly stabilizes the high energy  $K_2FeO_4$  electrode, and improves the energy storage capacity of super-iron batteries. For further improving the charge transfer of  $ZrO_2$  coated  $K_2FeO_4$  electrode, in our recent studies,  $Y_2O_3$ - $ZrO_2$  coatings were utilized to protect the  $K_2FeO_4$  electrode in an alkaline battery system [24], and the result demonstrates that the stability and charge transfer of  $Y_2O_3$ - $ZrO_2$  coated  $K_2FeO_4$  electrode are superior to that of  $ZrO_2$  coated  $K_2FeO_4$  electrodes. However, up till now, the  $K_2FeO_4$  electrodes have rarely been assembled into real batteries (including coin cells, cylindrical cells, etc.) for systematical investigation in the previous reports, although exploring the discharge performances of real batteries is very important for developing practical applications of alkaline super-iron batteries.

Based on our previous work, super-iron coin cells are assembled using a  $Y_2O_3$ - $ZrO_2$  coated  $K_2FeO_4$  electrode as the cathode and zinc foil as the anode. To obtain the optimal discharge performance of  $Y_2O_3$ - $ZrO_2$  coated  $K_2FeO_4$  cathodes, the preparation conditions of  $Y_2O_3$ - $ZrO_2$  coatings on  $K_2FeO_4$  electrodes were first investigated and determined by open module batteries, and then the application effects of coin cells were evaluated and observed.

## 2. Material and methods

### 2.1. Materials

$K_2FeO_4$  ( $\geq 60\%$ ) was purchased from Wuhan Galaxy Chemical Co. Ltd., and then recrystallized in an ice-bath before utilization ( $\geq 97\%$ ). Zirconium oxychloride ( $ZrOCl_2 \cdot 8H_2O$ ) and yttrium nitrate ( $Y(NO_3)_3 \cdot 6H_2O$ ) ( $\geq 99\%$ , Tianjin Bodhi Chemical Holding Co. Ltd.), ammoniacal water ( $NH_3 \cdot H_2O$ ) (AR grade, Kewei Corp. of Tianjin University), N-methyl pyrrolidone (NMP) and absolute ether (AR grade, Tianjin Chemical Reagent No. 1 Plant), acetylene black ( $\geq 99\%$ , Tianjin Jinqishi Chemical Co. Ltd.), and poly(vinylidene fluoride) (PVDF) ( $\geq 99\%$ , Chenguang Research Institute of Chemical Industry),  $MnO_2$  (AR grade, Changzhou Xinzhong Chemical Co. Ltd.) were purchased and used as-received. Typical coin cell package (CR2032) was used to assemble all coin cells.

### 2.2. Preparation of $Y_2O_3$ - $ZrO_2$ coated $K_2FeO_4$ electrodes

Details of the materials synthesis and electrode preparation were described in our previous publication [24]. Specific details are as follows: two drops of deionized water were dispersed in 20 mL ether by ultrasonic dispersion before  $ZrOCl_2 \cdot 6H_2O$  and  $Y(NO_3)_3 \cdot 6H_2O$  were added to the ether, and then stirred with 2.00 g recrystallized  $K_2FeO_4$  in the air for 0.5 h, the solution pH was adjusted with  $NH_3 \cdot H_2O$  during the above process, and the precipitation was dried by vertex suction at a set temperature overnight. Finally,  $K_2FeO_4$  with a  $Y_2O_3$ - $ZrO_2$  coating was obtained. The preparation of cathodes was completed through spreading a measured amount of slurry including the active mass mixed (coated or uncoated  $K_2FeO_4$  powder) with acetylene black (conductive matrix), PVDF (binder), and NMP (solvent) on clean nickel foam. The mass ratio of  $K_2FeO_4$  powder, acetylene black and PVDF is 80:15:5. Next, the as-prepared  $K_2FeO_4$  cathodes were pressed and dried at 333 K for several hours. The net weight of  $K_2FeO_4$  (including acetylene black and PVDF) on the electrode was about 0.25 g.

### 2.3. Fabrication of Open module battery and super-iron coin cell

The optimum preparation conditions of  $Y_2O_3$ - $ZrO_2$  coated  $K_2FeO_4$  electrodes were determined by open module batteries, the batteries consisted of coated or uncoated  $K_2FeO_4$  positive electrodes, non-woven polypropylene grafted separator and a zinc (Zn) foil anode,  $10 \text{ mol L}^{-1}$  KOH served as the electrolyte. In the process of fabricating coin cells, the separator and anode were the same as an open module battery,  $Y_2O_3$ - $ZrO_2$  coated  $K_2FeO_4$  electrode as cathode materials and electrolyte was the mixture of  $10 \text{ mol L}^{-1}$  KOH and carboxymethyl cellulose sodium. The coin cell packaging (CR2032) was used to assemble the super-iron coin cell. Stainless steel spacers in the packaging were used as current collectors. A disk of carbon fiber sheet (Spectracarb 2250) was placed between each stainless steel current collector in order to decrease the contact resistance ( $R_c$ ). The electrolyte was introduced to each electrode and sealed in the coin cell using a coin cell crimper by pressing at 1500 psi. The preparation of a  $MnO_2$  coin cell was similar to the  $K_2FeO_4$  coin cell.

### 2.4. Electrochemical properties measurement

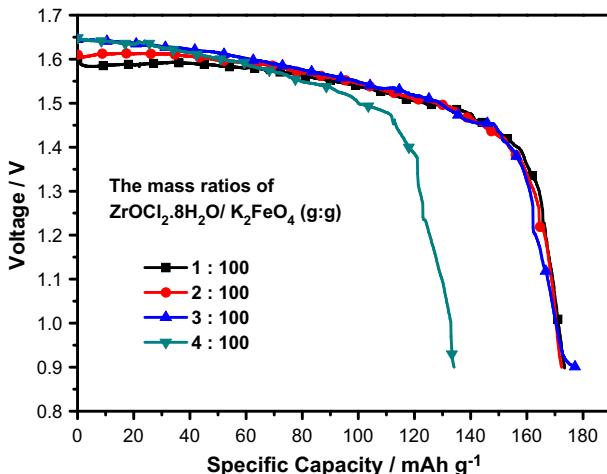
Electrochemical properties of as-assembled open module batteries and coin cells were studied at 298 K via a Land Battery Test System (CT2001A, Wuhan Jinnuo Electronic Ltd., China). The cut-off voltage was 0.9 V at the discharge current density of  $1 \text{ mA cm}^{-2}$ .

## 3. Results and discussion

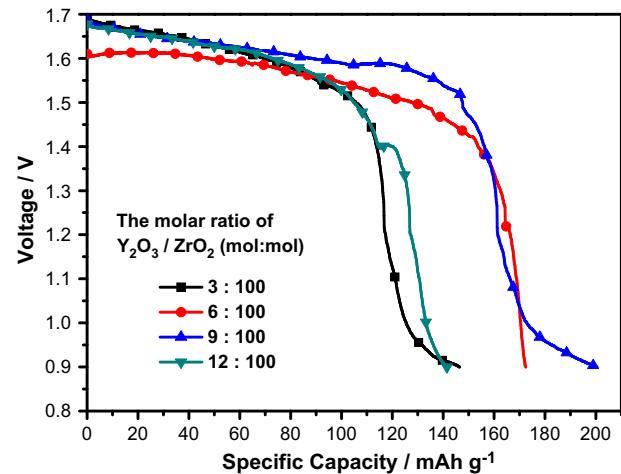
### 3.1. Effect of coating amount of $Y_2O_3$ - $ZrO_2$ on the discharge performance of $K_2FeO_4$ cathodes

In this work, it has been found that there are four preparation parameters jointly determining the discharge performance of  $K_2FeO_4$  cathodes, namely, the coating amount of  $Y_2O_3$ - $ZrO_2$ , the doping amount of  $Y_2O_3$  in  $Y_2O_3$ - $ZrO_2$ , the pH of the solution for preparing  $Y_2O_3$ - $ZrO_2$  coated  $K_2FeO_4$  and the temperature for drying  $Y_2O_3$ - $ZrO_2$  coated  $K_2FeO_4$ .

In order to determine the optimum coating amount of  $Y_2O_3$ - $ZrO_2$ , the effect of  $Y_2O_3$ - $ZrO_2$  coating with different quantities on the discharge specific capacity of  $Y_2O_3$ - $ZrO_2$  coated  $K_2FeO_4$  cathodes was investigated, and four different  $Y_2O_3$ - $ZrO_2$  coated  $K_2FeO_4$  cathodes were prepared by adjusting the mass ratio of



**Fig. 1.** Effect of coating amount of  $\text{ZrO}_2$  on the discharge specific capacity of  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes in  $10 \text{ mol L}^{-1}$  KOH electrolyte solution.



**Fig. 2.** Effect of coating amount of  $\text{Y}_2\text{O}_3$  on the discharge specific capacity of  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes in  $10 \text{ mol L}^{-1}$  KOH electrolyte solution.

$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$  (g:g) and the molar ratio of  $\text{Y}_2\text{O}_3/\text{ZrO}_2$  (mol:mol). Specifically, the mass ratios of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$  (g:g) are 1:100, 2:100, 3:100 and 4:100 respectively, at the molar ratio of  $\text{Y}_2\text{O}_3/\text{ZrO}_2$  (mol:mol) fixed to 6:100 in this investigation. The discharge profiles of as-prepared  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes at current density of  $1 \text{ mA cm}^{-2}$  are displayed in Fig. 1. It can be observed from Fig. 1 that when the mass ratio of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$  (g:g) is less than 3:100, the discharge specific capacity of the  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes shows a similar discharge tendency, namely, their discharge specific capacity are basically equal. This result suggests that a small amount of  $\text{ZrO}_2$  coating can enhance the discharge performance of  $\text{K}_2\text{FeO}_4$  cathodes obviously. However, when the mass ratio of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$  (g:g) is more than 4:100, the discharge specific capacity of  $\text{K}_2\text{FeO}_4$  cathodes indeed declines. Reason for this result is as follows: adding excessive zirconium salt can form a large number of zirconium salt colloids, which will increase the thickness of  $\text{ZrO}_2$  coatings on the surface of the  $\text{K}_2\text{FeO}_4$  cathode. Also, too thick films can become a barrier for the transfer of electrons and ions in the electrolyte to the  $\text{K}_2\text{FeO}_4$  cathode, causing the decline of the conductivity and discharge efficiency of  $\text{K}_2\text{FeO}_4$  cathode. Meanwhile, excessive zirconium salt will result in forming many new  $\text{ZrO}_2$  phases that accumulate among  $\text{K}_2\text{FeO}_4$  particles, which leads to increasing the resistance of electronic conduction, therefore, the discharge performance of the  $\text{K}_2\text{FeO}_4$  cathode decreases. Comparing the discharge specific capacity curves of  $\text{K}_2\text{FeO}_4$  cathodes in Fig. 1, to obtain the optimal discharge performance, the mass ratio of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$  (g:g) is confirmed between 2:100 and 3:100. In our work, 2.5:100 was chosen as the mass ratio of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$  (g:g) for the following research.

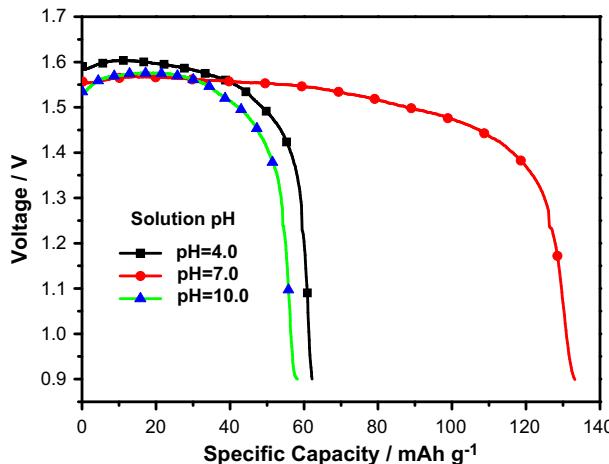
### 3.2. Effect of doping amount of $\text{Y}_2\text{O}_3$ in $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$ coatings on the discharge performance of $\text{K}_2\text{FeO}_4$ cathodes

The discharge performance of different  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes was investigated for confirming the optimum doping amount of  $\text{Y}_2\text{O}_3$  in  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coatings. In this study, the molar ratios of  $\text{Y}_2\text{O}_3/\text{ZrO}_2$  (mol:mol) are 3:100, 6:100, 9:100 and 10:100 (denoted as MR-3, MR-6, MR-9, MR-10 respectively) at the mass ratios of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$  (g:g) fixed to 2.5:100. The discharge curves of  $\text{K}_2\text{FeO}_4$  cathodes coated with  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  at a current density of  $1 \text{ mA cm}^{-2}$  are exhibited in Fig. 2. It can be seen that when the voltage is cut off at 0.9 V, the discharge specific

capacities of MR-3, MR-6, MR-9, MR-10 coated  $\text{K}_2\text{FeO}_4$  cathodes are  $146.4 \text{ mA h g}^{-1}$ ,  $172.3 \text{ mA h g}^{-1}$ ,  $200.4 \text{ mA h g}^{-1}$  and  $141.6 \text{ mA h g}^{-1}$ , respectively. These results indicate that the discharge performance of MR-6 and MR-9 coated  $\text{K}_2\text{FeO}_4$  cathodes presents a better result compared to that of MR-3 and MR-10 coated  $\text{K}_2\text{FeO}_4$  cathodes. According to the explanation provided by the previous report [24]: when the doping amount of  $\text{Y}_2\text{O}_3$  in  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coatings is too small, the affluent cubic  $\text{ZrO}_2$  which can sufficiently enhance the conductivity of  $\text{ZrO}_2$  will not be achieved and thus the advantage of  $\text{Y}_2\text{O}_3$  does not be fully realized; on the other hand, too much  $\text{Y}_2\text{O}_3$  in  $\text{ZrO}_2$  coatings may cause the conductivity of  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coatings to decline, as there are fewer oxygen vacancies contributing to conduction. Taking all factors into consideration, when the molar ratio of  $\text{Y}_2\text{O}_3$  and  $\text{ZrO}_2$  (mol:mol) is between 6:100 and 9:100,  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode attains the optimal discharge performance. In our work, the molar ratio of  $\text{Y}_2\text{O}_3$  and  $\text{ZrO}_2$  (mol:mol) was controlled at 9:100 for the subsequent research.

### 3.3. Effect of solution pH on the discharge performance of $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$ coated $\text{K}_2\text{FeO}_4$ cathodes

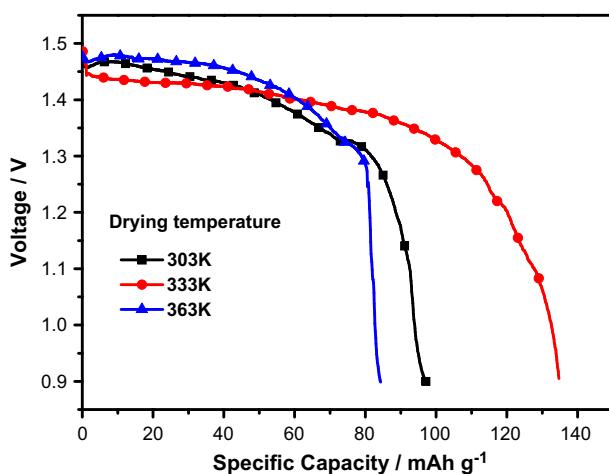
To determine the optimum pH of solution for preparing  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coatings, the solution pH of 4.0, 7.0 and 10.0 were chosen in this study and experimental results are demonstrated in Fig. 3. As seen in Fig. 3, when the discharge voltage reaches 0.9 V, the discharge specific capacity of  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode is  $133 \text{ mA h g}^{-1}$  under the pH of solution adjusted to 7. However, when the pH of solution is 4 or 10, the discharge specific capacities of  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes drop markedly. The phenomenon can be analyzed and explained using the effect of pH on the surface electric properties of  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  colloids. In the process of coating  $\text{K}_2\text{FeO}_4$  cathodes, when the solution pH is low, the  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  colloid is difficult to form. Consequently, there is not enough  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coating to protect  $\text{K}_2\text{FeO}_4$  cathode; in contrast, when the solution pH is high, the formation of  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  colloid is too fast, resulting in  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  colloid unevenly distributed on the surface of the  $\text{K}_2\text{FeO}_4$  cathode. Hence, neither case mentioned above can be beneficial for  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  coatings well distributed on  $\text{K}_2\text{FeO}_4$  cathodes. Therefore, the suitable pH of solution is between 7 and 8. In this work, we chose 7 as the solution pH for the following research.



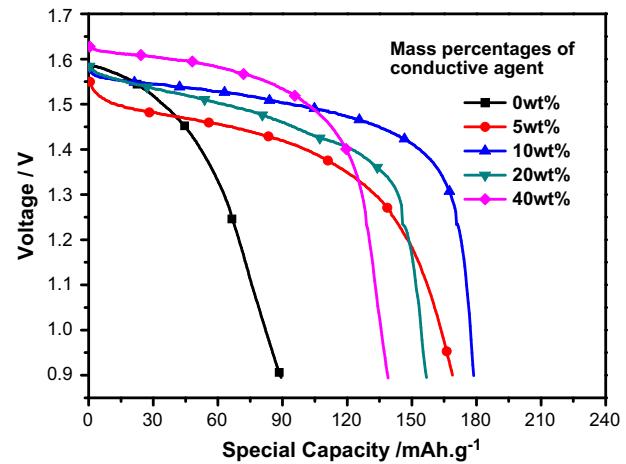
**Fig. 3.** Effect of solution pH on the discharge specific capacity of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes in the coating process.

### 3.4. Effect of drying temperature on the discharge performance of $\text{Y}_2\text{O}_3\text{-ZrO}_2$ coated $\text{K}_2\text{FeO}_4$ cathodes

For investigating the effect of drying temperature on the discharge performance of the  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode, the drying temperature of 303 K, 333 K and 363 K were chosen in this investigation and corresponding results are shown in Fig. 4. When the discharge voltage reaches 0.9 V, the discharge specific capacities of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes are  $97.1 \text{ mA h g}^{-1}$  and  $135 \text{ mA h g}^{-1}$  under the drying temperature of 303 K and 333 K, respectively. Surprisingly, the discharge specific capacity of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode declines to  $84.2 \text{ mA h g}^{-1}$  when drying temperature rises to 363 K (as seen in Fig. 4). That is to say, within a certain temperature range, the discharge performance can be improved by raising the drying temperature; however, increasing the drying temperature continuously will make the discharge specific capacity of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes decrease abruptly. The reason is that  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes can be rapidly decomposed when temperature surpasses 353 K. Therefore, a drying temperature less than 353 K should be reasonable in this work. Through observing the discharge performance of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes, the drying temperature fixed



**Fig. 4.** Effect of drying temperature on the discharge specific capacity of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes.



**Fig. 5.** Discharge curves of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes with different amounts of conductive agent.

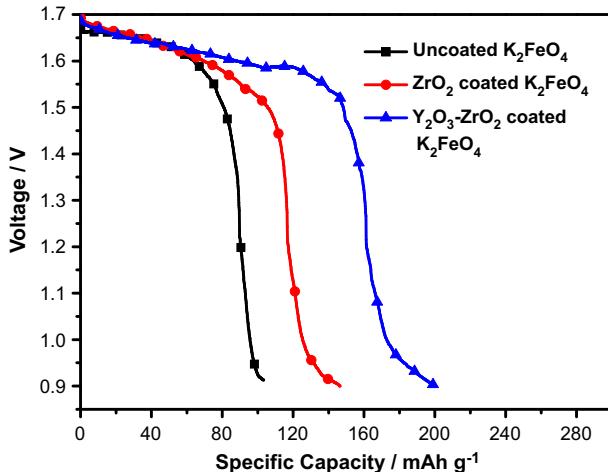
to between 323 and 343 K is appropriate. In our work, 333 K was chosen as a fitting drying temperature for the following research.

### 3.5. Effect of conductive agent on the discharge performance of $\text{Y}_2\text{O}_3\text{-ZrO}_2$ coated $\text{K}_2\text{FeO}_4$ cathodes

The effect of conductive agent for preparing  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes on the discharge capability of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes was investigated. In this investigation, the mass percentages of conductive agent (acetylene black) in the  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes were 0 wt.%, 5 wt.%, 10 wt.%, 20 wt.% and 40 wt.%, respectively. It can be observed from Fig. 5, when no conductive agent was added into cathode (0 wt.%), the discharge specific capacity of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode is only  $88.9 \text{ mA h g}^{-1}$ , and the discharge voltage reduces quickly during the discharge process for serious positive polarization. Obviously, appropriately increasing the content of conductive agent can remarkably improve the discharge specific capacity of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes. The conductive agent facilitates the charge transfer among the  $\text{K}_2\text{FeO}_4$  particles and decreases the resistance of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes. On the other hand, the conductive agent ensures sufficient electrolyte to be used in the cathode and delays the positive polarization. However, too much conductive agent can gradually drop down the discharge specific capacity of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode (as shown in Fig. 5). Increasing content of conductive agent thickens the as-prepared cathodes significantly, hindering the contact between active mass ( $\text{K}_2\text{FeO}_4$ ) and electrolyte, meanwhile it also increases the cathode polarization. Therefore both effects negatively influence the discharge performance of the  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode. In this work, the appropriate content of conductive agent for preparing  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes ranged between 10% and 15%.

### 3.6. Discharge performance analysis of $\text{Y}_2\text{O}_3\text{-ZrO}_2$ coated $\text{K}_2\text{FeO}_4$ cathodes in open module battery

In order to validate the effect of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coatings on  $\text{K}_2\text{FeO}_4$  cathodes (prepared under the optimum conditions), uncoated and  $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes were also prepared for comparison purpose. The discharge specific capacities curves of  $\text{ZrO}_2$  coated and uncoated  $\text{K}_2\text{FeO}_4$  cathodes as well as  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathodes are comparatively presented in Fig. 6. It can be observed from Fig. 6 that when the discharge voltage reaches 0.9 V, the discharge specific capacities of  $\text{ZrO}_2$  and  $\text{Y}_2\text{O}_3\text{-ZrO}_2$



**Fig. 6.** The discharge performance curves of uncoated  $\text{K}_2\text{FeO}_4$  cathode and coated  $\text{K}_2\text{FeO}_4$  cathodes in open module batteries.

coated  $\text{K}_2\text{FeO}_4$  cathodes are  $146.5 \text{ mA h g}^{-1}$  and  $200.4 \text{ mA h g}^{-1}$  respectively, in contrast to the specific capacity of  $103.4 \text{ mA h g}^{-1}$  from the uncoated  $\text{K}_2\text{FeO}_4$  cathode. Apparently, the discharge specific capacity of the  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode is much higher than that of the uncoated  $\text{K}_2\text{FeO}_4$  cathode. Alternatively, it should be noted that the discharge specific capacity of  $\text{ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode is not remarkably improved compared with that of the uncoated  $\text{K}_2\text{FeO}_4$  cathode. The reason is that although  $\text{ZrO}_2$  coatings can stabilize  $\text{K}_2\text{FeO}_4$  cathode in alkaline electrolyte by preventing  $\text{K}_2\text{FeO}_4$  cathode from forming Fe (III) overlayers which can accelerate the decomposition of  $\text{K}_2\text{FeO}_4$  electrodes, the conductive property of pure  $\text{ZrO}_2$  is very poor, resulting that pure  $\text{ZrO}_2$  coating becomes a barrier for ions exchange and charge transfer in alkaline electrolyte. It is generally recognized that the addition of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  can improve the conductivity of  $\text{ZrO}_2$  coatings [24]. Therefore, the employment of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coatings layer not only can protect  $\text{K}_2\text{FeO}_4$  cathode from forming Fe (III) overlayers, but also can facilitate the ions transportation and charge transfer in alkaline electrolyte. Consequently, the specific capacity of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode is obviously enhanced (see Fig. 6).

### 3.7. Effect of temperature on the discharge performance of $\text{K}_2\text{FeO}_4$ coin cell

To examine the applicability of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  electrodes under practical work conditions,  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  electrodes were assembled into coin cells (denoted as  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cell). Fig. 7 is the digital image of an as-prepared super-iron coin cell. The effect of temperature on the discharge performance of  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cell was investigated. Fig. 8 shows the discharge curves of  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cells at 293 K, 313 K and 333 K. As seen in Fig. 8, the discharge curve of  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cell at 293 K is smooth and stable. However, when the surrounding temperature is 313 K or 333 K, the discharge curves of  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cells fluctuate severely; besides, the voltage linearly declines when discharged for a certain time. The phenomenon is partly caused by external factors, specifically, the experimental temperature fluctuations and changes around the set temperature, resulting in the discharge voltage of  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cell is unstable during the discharge process. More importantly, the active mass ( $\text{K}_2\text{FeO}_4$ ) of cathode in  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cell easily decomposes under high temperature, leading to the discharge voltage appear a sudden drop during the

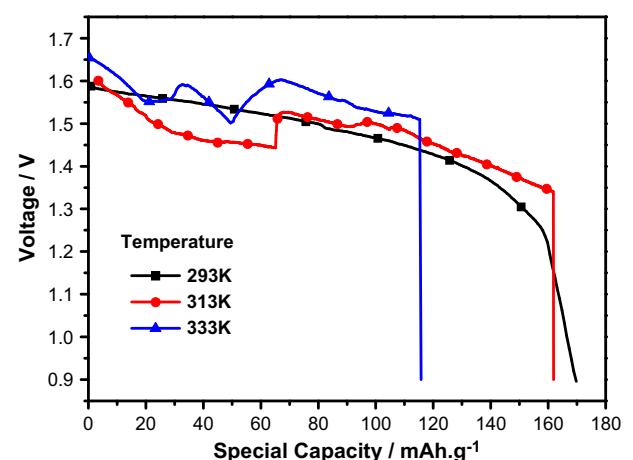


**Fig. 7.** Digital image of  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cells.

discharge process. Therefore, the reasonable work temperature for  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cell should below 313 K.

### 3.8. Analysis of discharge performance of coin cells

To compare the discharge performance of  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cell with a conventional  $\text{Zn/MnO}_2$  battery,  $\text{MnO}_2$  electrode material was also assembled into a coin cell (denoted as  $\text{Zn/MnO}_2$  coin cell). Fig. 9 exhibits the discharge curves of  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cell and  $\text{Zn/MnO}_2$  coin cell. As shown in Fig. 9, when the discharge voltage is cut off to 0.9 V, the discharge specific capacity and specific energy of  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cell are  $169.8 \text{ mA h g}^{-1}$  and  $201.9 \text{ Wh kg}^{-1}$  respectively, obviously higher than that of  $\text{Zn/MnO}_2$  coin cell. In addition, the discharge voltage plateau of  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cell is more stable than that of  $\text{Zn/MnO}_2$  coin cell, and the discharge voltage of the  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cell is about 0.25 V higher than that of  $\text{Zn/MnO}_2$  coin cell. Therefore, it can be concluded that the  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cell is superior to the  $\text{Zn/MnO}_2$  coin cell in terms of discharge performance. Moreover,  $\text{K}_2\text{FeO}_4$  cathode is more environmental-friendly than the  $\text{MnO}_2$  cathode and the raw material of  $\text{K}_2\text{FeO}_4$  cathode is more abundant than that of the  $\text{MnO}_2$  cathode.



**Fig. 8.** Effect of work temperature on the discharge specific capacity of  $\text{Zn/YZ-K}_2\text{FeO}_4$  coin cells.

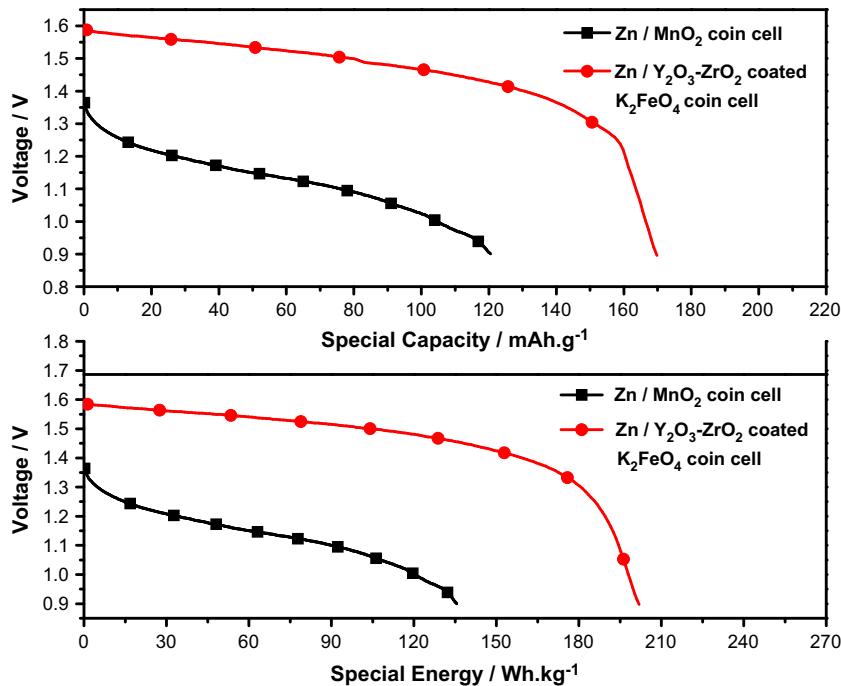


Fig. 9. The discharge performance curves of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  coin cells and  $\text{Zn}/\text{MnO}_2$  coin cell.

#### 4. Conclusions

The paper presents a novel method utilizing  $\text{Y}_2\text{O}_3$  doped  $\text{ZrO}_2$  as a protecting coating to improve the stability and charge transfer of  $\text{K}_2\text{FeO}_4$  electrode in alkaline electrolytes. Preparation conditions of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coating on  $\text{K}_2\text{FeO}_4$  electrode have been investigated, with the optimum coating conditions identified as below: the mass ratio of  $\text{ZrOCl}_2\text{-8H}_2\text{O}/\text{K}_2\text{FeO}_4$  (g:g) from between 2:100 and 3:100, the molar ratio of  $\text{Y}_2\text{O}_3/\text{ZrO}_2$  (mol:mol) from between 6:100 and 9:100, the coating pH is adjusted to be 7 or 8, the drying temperature of 333 K and 10–15% content of conductive agent for preparing  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  electrode. The discharge tests with an open module battery show that the discharge specific capacity of a  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  electrode (prepared under optimum preparation conditions) is obviously higher than that of an uncoated  $\text{K}_2\text{FeO}_4$  electrode. Alternatively, a super-iron coin cell is assembled using a  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  electrode as cathode and zinc foil as the anode. The coin cell with a  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  coated  $\text{K}_2\text{FeO}_4$  cathode exhibits a discharge specific capacity of  $169.8 \text{ mA h g}^{-1}$  and discharge specific energy of  $201.9 \text{ W h kg}^{-1}$ , respectively. Discharge result shows that the electrochemical properties of  $\text{Zn}/\text{YZ}-\text{K}_2\text{FeO}_4$  coin cell are superior to that of  $\text{Zn}/\text{MnO}_2$  coin cell. Therefore, with a view point for enhancing energy storage density; mitigating environmental pollutants, and improving the sustainability of electrode material utilization of primary batteries; the alkaline super-iron battery is expected to become a novel energy resource and is likely to replace the present primary batteries in various electronic devices.

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